

ISSN 0840-8440

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE 1988

November 28 and 29, 1988

Royal York Hotel

Toronto, Ontario

SESSION D

ANALYTICAL METHODS

Sponsored by

Research and Technology Branch

Environment Ontario

Ontario, Canada

AASG

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## DP9

APPLICATIONS OF FLOW INJECTION TECHNOLOGY TO ICP-MS  
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Inductively coupled plasma mass spectrometry (ICP-MS) is now a well-established technique for elemental analysis. Excellent limits of detection, accuracy and precision can be obtained using pneumatic nebulization.

Certain environmental studies conducted at the Ontario Ministry of the Environment require elemental instrument sensitivities beyond the detection power of conventional ICP-MS. In addition, small sample size and high concentrations of dissolved solids may hinder the development of reliable methods for such studies.

To enhance the analytical capabilities of ICP-MS, many different sample introduction devices have replaced conventional nebulization. These include hydride generation (1), direct sample insertion (2), laser ablation (3), and electro-thermal vaporization (4).

Flow Injection Analysis (FIA) is a unique and versatile type of continuous flow analysis that is finding increasing use in laboratories throughout the world (5). Detection devices used for flow injection include colorimetry, AAS, and ICP-AES with the development of these techniques being well-documented (6,7).

Flow injection ICP-MS was first investigated by Houk and Thompson (8). They used this technique for isotope ratio determinations of Mg and Ni and succeeded in obtaining an isotope ratio precision of 1-3% R.S.D. A subsequent publication reported simultaneous multi-element concentration determinations for four elements (9). Most recently, Ebdon et al (10) applied flow injection to ICP-MS for trace metal analysis of biological reference materials for lead and to obtain zinc isotope ratios of microlitre samples of blood.

The advantages of using flow injection ICP-MS are:

1. Small sample size (typically in the microlitre range).
2. A reduction in matrix effect.
3. Increased detection power (with in-line preconcentration).

This paper will discuss the characteristics of flow injection as applied to ICP-MS as an alternative sample introduction system.

The basic principle of flow injection is quite simple. A discrete volume of liquid sample is injected into a carrier stream which flows to a detector. The injection is accomplished by the use of a rotary valve. The carrier stream flowrate is maintained by a precision peristaltic pump. The sample "plug" is injected into the carrier stream and a transient signal appears at the detector.

The flow injection apparatus used in this study is a Lachat rotary valve model 1000 - 600. This is an electro-mechanical valve that is triggered automatically by TTL pulses generated in the central processing unit of the ICP-MS computer. Liquid flow is controlled by a peristaltic pump (Gilson Minipuls - 2). The detector used is a Sciex Elan model 250 ICP-MS system connected to a stand alone personal computer for data handling.

Flow injection produces a transient signal. Transient signal measurement is accomplished by using a special transient measurement program in the Elan software. Originally this software was devised for an electro-thermal vaporization device. Utilization for the flow injection apparatus was quite straightforward, using the various ramp voltage timing sequences for the rotary valve. Automatic triggering of the data acquisition system is also possible using this software program. This allows for very reproducible results when measuring several peaks.

In addition to controlled triggering, appropriate dwell times must be used in order to obtain good precision. Dwell time is the length of time the computer is resident on a selected mass peak while acquiring data. Optimum dwell time will vary depending on the number of peaks and the transient signal duration. For single element analysis, experiments have shown that a 300 ms dwell time is optimum. At this dwell time the precision obtained after the measurement of seven different injections of a 100 ug/l aqueous Pb standard was approximately 3% R.S.D.

The residence time of a transient signal produced by flow injection will vary depending on the extent of dispersion. There are two modes of physical dispersion: convection, and radial molecular diffusion. The effects of each of these depend on a number of key experimental parameters (carrier stream flowrate, tubing size from the injector unit to the detector and sample loop volume). Various response curves have been produced for each of these parameters.

Once a set of response curves has been created, this information can be used to find optimum parameters. This will enable the utilization of dilution caused by dispersion to minimize matrix effects.

After optimizing this particular system, a significant reduction in matrix effects was observed compared with continuous nebulization. However, the detection limits for the analytes investigated degraded by a factor of 5. Detection limits will vary with the extent of dispersion.

With conventional nebulizers, samples with high amounts of dissolved solids (>1%) form oxides in the plasma and tend to "clog" the sampling orifice of the ICP-MS. Experiments in this study have shown that using flow injection to introduce high dissolved solids solutions produces far less oxide. Therefore orifice "clogging" is substantially reduced.

At present trace analysis of uranium in water, soils, vegetation, air, and dustfall is done by conventional ICP-MS. Trace uranium analysis in an industrial waste matrix poses a problem for conventional ICP-MS due to the potential of high dissolved solids in the matrix. Preliminary work on the development of a method to estimate the concentrations of uranium by flow injection ICP-MS is in progress. Initial results indicate that minimum matrix effects are seen, and that the data are precise and accurate.

Flow injection in general is very versatile and offers a number of in-line sample pretreatment processes. Preconcentration is one of them (11). With an ever increasing demand to gain lower detection limits, preconcentration with flow injection ICP-MS offers a potential of detection power in the parts per quadrillion range.

Sample speciation studies are also possible. Separation can also be accomplished in-line with a flow injection unit.

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